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BATCH COOKABLE MODIFIED HIGH AMYLOSE STARCHES AND THEIR USE IN PAPER SIZING APPLICATIONS

Abstract:

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(57) Abstract: The present invention pertains to pregelatinized modified, high amylose starches that are batch cookable to a uniform, substantially particle-free dispersion at atmospheric pressures and the process of preparing such starches in an extruder. Such pregelatinized, modified, high amylose starches are useful in a variety of applications without the need for jet cooking. In addition, such starches are readily dispersible at high solids to provide uniform formulations and are substantially non-retrograded. Further, such starches provide improved surface sizing agents which use results in the preparation of paper which is characterized by improved water resistance, reduced porosity, and other size properties.

BATCH COOKABLE MODIFIED HIGH AMYLOSE STARCHES AND THEIR
USE IN PAPER SIZING APPLICATIONS

5

BACKGROUND OF THE INVENTION

This invention relates to a batch cookable, modified high amylose starch and the method of making such starch. Further, this invention relates to the use 10 of such starches in dispersion to improve the process of surface sizing paper and paperboard and the resulting sized paper product.

Paper and paperboard are often sized with various materials for the purpose of increasing their strength, their resistance to picking and scuffing, and their 15 resistance to undue penetration of water, organic solvents, oils, inks and various types of aqueous solutions as well as for the purpose of improving their smoothness and optical characteristics. When sizing materials are applied to the surface of a web or sheet in order to cement the surface fibers to the body of the paper and to modify the sheet surface, the process is 20 known as external or surface sizing; the latter process being quite distinct from an internal sizing process wherein sizing agents are admixed with the pulp slurry prior to its being converted into web or sheet form.

Among the various materials that have been utilized as surface sizing agents 25 are included conventional and modified starches, polyvinyl alcohol, cellulosic derivatives, gelatin, rosin, proteins such as casein, and synthetic polymers. Although these materials are effective to various degrees under certain

conditions, their use is nonetheless subject to one or more limitations. For example, it is often necessary to utilize high concentration levels of such sizes in order to achieve the desired strength and aqueous holdout characteristics. Since it is known that the opacity and brightness of the base paper sheet decrease in proportion to the amount of size that is applied thereto, a direct result of the required use of such high concentration levels is a reduction in the optical properties of the treated paper. Furthermore, the use of such high concentration levels makes the sizing of specialty papers economically unattractive inasmuch as high cost, quality sizes, e.g. gelatin, animal glue and casein, are usually utilized for such purposes. In addition, certain sizing agents known in the art impart relatively poor water resistance and must be used in conjunction with insolubilizing agents in order that satisfactory water resistance is obtained.

15 Hydrophobically substituted high amylose starches have been utilized as surface size agents in the preparation of photographic paper, for example see US Patent No. 5,254,450. However, this patent teaches the need for high temperature to completely disperse the starch granules in order to obtain the benefits of improved resistance to oxygen permeability (gas impermeable films) resulting in increased stability of the dye system.

20 High amylose starches are well known in the art and used in a variety of applications including food and beverages, paper and paper board, pharmaceuticals and nutraceuticals, and personal care products. They are used for the desirable functionality, including such properties as strong gel strength, good film forming with films which are water resistant and gas impermeable, and excellent surface properties, ie smoothness and strength.

However, high amylose starches are difficult to cook out and need high pressure in order to reach the elevated temperatures to do so, ie. by jet cooking. This characteristic makes high amylose starches undesirable in 5 many applications, as the starch must be cooked out prior to using it. The necessary extra processing makes high amylose starches commercially undesirable to many manufacturers not only for the additional processing time, but also because the equipment is expensive and not readily available. Also, high amylose starches can undergo a gel formation or crystallization 10 (retrogradation) that leads to instability after dispersion and during application. This instability can be overcome by chemical modification, but highly substituted materials exhibit reduced performance compared to unmodified products in that they have poor water resistance and form poor films and weak gels.

15

To overcome the need for cooking under pressure, some starch companies have provided pregelatinized high amylose starches by jet cooking the starch and then spray drying the gelatinized starch. Due to the quick retrogradation 20 of high amylose starches, this is preferably accomplished by a continuous coupled process in which the jet cooked, high amylose starch is immediately conveyed and introduced under elevated temperature and pressure into the spray drier as described in US 5,131,953.

Although such pregelatinized high amylose starches are sufficiently 25 pregelatinized for most applications, due to their fine particle size it is very difficult to provide the high solids, uniform formulations necessary for many applications, including those typically used in paper coatings and surface

size. The fine particles tend not to readily disperse, resulting in clumps and formation of "fish eyes" instead of a uniform dispersion.

Further, unless prepared properly using the coupled process, retrogradation
5 can occur resulting in insoluble crystalline particles. Such crystalline particles
are detrimental to many applications, particularly papermaking in which the
crystalline particles result in very non-uniform surface properties, a major
concern to papermakers.

10 Surprisingly, it has now been discovered that modified, high amylose
starches may be pregelatinized in an extruder to provide high amylose
starches that are batch cookable to a uniform, substantially particle-free
dispersion at atmospheric pressures. Such pregelatinized, modified, high
amylose starches are useful in a variety of applications without the need for
15 jet cooking. In addition, such starches are readily dispersible at high solids to
provide uniform formulations and are substantially non-retrograded. Further,
such starches provide improved surface sizing agents which use results in
the preparation of paper which is characterized by improved water resistance,
reduced porosity, and other size properties.

20

SUMMARY OF THE INVENTION

The present invention pertains to pregelatinized modified, high amylose
starches that are batch cookable to a uniform, substantially particle-free
dispersion at atmospheric pressures and the process of preparing such
25 starches in an extruder. Such pregelatinized, modified, high amylose
starches are useful in a variety of applications without the need for jet
cooking. In addition, such starches are readily dispersible at high solids to

provide uniform formulations and are substantially non-retrograded. Further, such starches provide improved surface sizing agents which use results in the preparation of paper which is characterized by improved water resistance, reduced porosity, and other size properties.

5

As used herein, the terms paper and paperboard include sheet-like masses and molded products made from fibrous cellulosic materials which may be derived from both natural and synthetic sources. Also included are sheet-like masses and molded products prepared from combinations of cellulosic and 10 non-cellulosic materials derived from synthetics such as polyamide, polyester and polyacrylic resin fibers as well as from mineral fibers such as asbestos and glass.

DETAILED DESCRIPTION OF THE INVENTION

15 The present invention pertains to pregelatinized modified, high amylose starches that are batch cookable to a uniform, substantially particle-free dispersion at atmospheric pressures and the process of preparing such starches in an extruder. Such pregelatinized, modified, high amylose starches are useful in a variety of applications without the need for jet cooking. In addition, such starches are readily dispersible at high solids to 20 provide uniform formulations and are substantially non-retrograded. Further, such starches provide improved surface sizing agents which use results in the preparation of paper which is characterized by improved water resistance, reduced porosity (as measured by TAPPI T460, 11/92), and other size 25 properties.

All high amylose starches and flours (hereinafter "starch") may be suitable for use herein and may be derived from any native high amylose source. A native starch as used herein, is one as it is found in nature. Also suitable are starches derived from a plant obtained by standard breeding techniques including crossbreeding, translocation, inversion, transformation or any other method of gene or chromosome engineering to include variations thereof. In addition, starch derived from a plant grown from artificial mutations and variations of the above generic composition which may be produced by known standard methods of mutation breeding are also suitable herein.

10

Typical sources for the starches are cereals, tubers, roots, legumes and fruits. The native source can be corn, pea, potato, sweet potato, banana, barley, wheat, rice, sago, amaranth, tapioca, arrowroot, canna, sorghum. High amylose starch, as used herein, is intended to mean any starch containing at least 40% amylose, or in the case of rice starch at least 27% amylose.

The high amylose starches of the present invention must be chemically modified. Such chemical modifications are intended to include without limitation acetylated and organically esterified starches, etherified starches such as hydroxyethylated and hydroxypropylated starches, phosphorylated and inorganically esterified starches, cationic, anionic, nonionic, and zwitterionic starches, and succinate and substituted succinate derivatives of starch, particularly etherified and esterified starches. More particularly, suitable starches include those modified by octenylsuccinic acid, dodecylsuccinic acid, propylene oxide, and quaternary amines including 3-chloro-2-hydroxypropyl-N,N,N-trimethylammonium chloride. Such

modifications are known in the art, for example in Modified Starches: Properties and Uses, Ed. Wurzburg, CRC Press, Inc., Florida (1986).

- The starch must be modified so that it will remain substantially non-retrograded in dispersion for a time sufficient to process the starch, ie. size paper. However, the starch must not be modified to such a degree that the modification will interfere with the linear nature of the starch and negate the desirable characteristics associated with such linearity, ie. film forming.
- 10 The amount of chemical modification is measured by DS, or degree of substitution. As used herein, DS is intended to mean the number of OH groups per anhydroglucose unit available for reactivity; therefore the DS range for unsubstituted to totally substituted starch materials will be 0 to 3. The starch will typically have a minimum DS of at least about 0.01, particularly about 0.03. Further, the starch will typically have a maximum DS of no more than about 0.5, particularly about 0.2.
- 15

The starch may further be converted, either prior to or after the chemical modification. Conversion products include fluidity or thin-boiling starches prepared by oxidation, enzyme conversion, acid hydrolysis, heat and or acid dextrinization, thermal and or sheared products. Reduction of native starch molecular weight may be desirable to overcome any deficiencies in viscosity or rheology, and can be used to control the amount of material applied to the paper surface. However, due to the typically lower viscosity obtained by high amylose starches, conversion products are not necessary for many applications.

Any starch or starch blends having suitable properties for use herein may be purified, either before or after any modification or conversion, by any method known in the art to remove starch off flavors, odors, or colors that are native to the starch or created during processing. Suitable purification processes for 5 treating starches are disclosed in the family of patents represented by EP 554 818. Alkali washing techniques are also useful and described in the family of patents represented by U.S. 4,477,480 and 5,187,272.

The starches of the present invention are produced by extrusion. The starch 10 is extruded under conditions sufficient to allow gelatinization (substantial destruction of the starch granule).

In the extrusion process, the total moisture content of the high amylose starch prior to extrusion should be at a level of no more than about 21%, particularly 15 about 17%, by weight, based on the dry weight of the starch. Total moisture or water content includes both the residual moisture of the starch and the amount of water fed to the extruder. Typically, high amylose starch contains about 9 to 14% residual moisture. Enough water must be present to allow the material to be processed, mixed and heated to the desired temperatures. 20 While some water may be added to the extruder, only an amount which will bring the total moisture level to no more than about 25% is typically added. Accordingly, while the total moisture content that is used for carrying out the process may vary somewhat, depending on the starch material used (base and modification) and other process variations, a range of from about 13 to 25 25%, particularly from about 15 to 22% and more particularly from about 16 to 19% by weight, will generally be suitable.

During the extrusion process, the temperature of the material in the extruder will be increased to reach about 150°C to 250°C, dependent upon type of starch and its modification. This temperature must be maintained in at least the section of the extruder closest to the die and just before the material leaves the extruder. The die is positioned at the point or location at the end of the extruder from which the extruded material exits the apparatus into the ambient air. Depending on the particular material being processed and the process parameters, this temperature can vary somewhat within the noted range and particularly will be from about 150°C to 210°C. When the starch is modified by an ether, the temperature is typically from about 160°C to 200°C, whereas when the starch is modified by an ester the temperature is typically from about 170°C to 210°C, at least in the section of the extruder closest to the die. By maintaining these conditions in the extruder, the material upon leaving the die and extruder outlet into the open air, expands and cools to form an expanded starch product.

The apparatus used in carrying out this process may be any screw-type extruder. While a single- or twin-screw extruder may be used, a twin-screw extruder is generally more suitable. Such extruders will typically have rotating screws in a horizontal cylindrical barrel with an entry port mounted over one end and a shaping die mounted at the discharge end. When twin screws are used, they may be co-rotating or counter-rotating, and intermeshing or nonintermeshing. Each screw will comprise a helical flight or threaded section and typically will have a relatively deep feed section followed by a tapered transition section and a comparatively shallow constant-depth meter section. The screws, which are motor driven, generally fit snugly into the

cylinder or barrel to allow mixing, heating and shearing of the material as it passes through the extruder.

Control of the temperature along the length of the extruder barrel is important
5 and is controlled in zones along the length of the screw. Heat exchange means, typically a passage, such as a channel, chamber or bore located in the barrel wall, for circulating a heated media such as oil, or an electrical heater such as calrod or coil type heaters, is often used. Additionally, heat exchange means may also be placed in or along the shaft of the screw
10 device.

Variations in any of the elements used in the extruder may be made as desired in accordance with conventional design practices in the field. A further description of extrusion and typical design variations can be found in
15 Encyclopedia of Polymer Science and Engineering, Vol. 6, 1986, pp. 571 to 631.

The resultant extruded starch can be ground to any particle size(s) suitable for use in the desired application using techniques and equipment known in
20 the art. For example, when used for paper sizing or other applications in which it is desired to hydrate and disperse the starch in hot water, the extruded starch should not be of a fine particle size and is typically ground to a mean particle size of no less than about 60 microns, particularly no less than about 100 microns. It is important in this instance to use grinding
25 equipment which does not produce significant heat such that the starch melts and case hardens which would interfere with hydration and dispersion; for example air classified grinding may be used.

The resultant starches are pregelatinized and characterized by their ability to readily disperse and hydrate in hot water without substantial clumping or formation of "fish eyes." Thus, manufacturers may use the starch without the 5 necessity of jet cooking. The resultant starches provide uniform, substantially particle-free formulations and are substantially non-retrograded (non-crystalline). The resultant starch acts similarly to jet cooked high amylose starches in applications and are superior over starches that are pregelatinized using other methods.

10

The starches may be used in a variety of applications including food and beverages, paper and paper board, pharmaceuticals and nutraceuticals, and personal care products. Food and beverages is intended to include, but is not limited to, sauces and gravies, salad dressings and mayonnaises, 15 cultured products such as yogurts and sour cream, puddings, desserts, baked goods, instant foods, soups, candies including gelled candies, batters, breadings, and coatings, and beverages, particularly baked goods, gelled candies, batters, breadings, and coatings. Pharmaceuticals and nutraceuticals is intended to include, but is not limited to tablets, diabetic 20 compositions, and nutritional bars and drinks. Personal care products is intended to include, but is not limited to creams and lotions, mousses and gels, hair care products, and deodorants.

The starches of this invention may be added in the dry state, or in a 25 substantially particle-free dispersion. Such dispersion may typically be prepared by adding the starch to hot water with agitation or stirring.

The starches of this invention are particularly useful for the sizing of paper prepared from all types of both cellulosic and combinations of cellulosic with noncellulosic fibers. The hardwood or soft wood cellulosic fibers that may be used include bleached and unbleached sulfate (kraft), bleached and
5 unbleached sulfite, bleached and unbleached soda, neutral sulfite semi-chemical, chemi-groundwood, groundwood, and any combination of these fibers. These designations refer to wood pulp fibers which have been prepared by means of a variety of processes which are used in the pulp and paper industry. In addition, synthetic cellulose fibers of the viscose rayon or
10 regenerated cellulose type can also be used, as well as recycled waste papers from various sources.

All types of paper dyes and tints, pigments and fillers may be added to the paper which is to be sized in accordance with this invention. Such materials
15 include without limitation clay, talc, titanium dioxide, calcium carbonate, calcium sulfate, and diatomaceous earths. The paper can contain other additives, including rosin and alum and other internal sizes. Other surface sizing compounds as well as pigments, dyes and lubricants can also be used in conjunction with the size blends described herein.

20

The starch size dispersion is applied to a previously prepared paper or paperboard web by means of any conventional surface sizing technique. These techniques include, but are not limited to, size press, tub, gate roll applicators and calender stack sizing procedures. Thus, for example, in a
25 size press technique, surface sizing is accomplished by passing the web of paper between a pair of press rolls wherein the lower roll of the pair is rotating in a batch of the sizing dispersion. The surface of this roll picks up size and

deposits it on the lower surface of the web. If desired, sizing may also be applied to the upper surface of the web by spraying it into the nip formed between the web and the upper roll, or by spraying it against the surface of the upper roll and allowing it to accumulate on the upper surface of the web 5 as it enters the press. The sized webs are then dried by means of any conventional drying operation selected by the practitioner.

The starches of this invention are ordinarily employed in amounts to provide a size concentration ranging from about 0.25 to 15.0% of the weight of the 10 finished dry paper. Within this range, the precise amount which is used will depend for the most part upon the type of pulp which is being utilized, the specific operating conditions, as well as the particular end use for which paper is destined.

15 The use of the present starches as surface sizing agents results in paper characterized by similar improved water resistance and reduced porosity to that obtained using jet cooked modified high amylose starches.

EXAMPLES

20 The following examples are presented to further illustrate and explain the present invention and should not be taken as limiting in any regard. All percents/parts used are on a weight/weight basis unless otherwise noted.

The following base starches were used:

25 70 HA starch = 70% high amylose starch, commercially available as HYLON® VII from National Starch and Chemical Company

- 70 HA/OSA starch = Octenylsuccinic anhydride (OSA) treated 70% high amylose starch modified prepared as follows. 500 grams of 70% high amylose starch were slurried in 750 ml water. The pH was adjusted to 7.5 using 3% sodium hydroxide. 15 grams of octenylsuccinic anhydride (OSA) were added in one-third increments every 5 thirty minutes while maintaining the pH at 7.5 using 3% sodium hydroxide and constant agitation. The starch was then filtered out and washed with 750 ml water. The starch was then reslurried in 500 ml water and the pH adjusted to 5.5 with 3:1 hydrochloric acid. The starch was then filtered, washed with 750 ml water, and air dried.
- 10 70 HA/PO starch = Propylene oxide (PO) treated 70% high amylose starch prepared as follows. 1000g of 70% high amylose starch were slurried in 1500g water. To this slurry was added 250g sodium sulfate. The pH was then adjusted to 11-12 by addition of 500g of a 3% sodium hydroxide solution. 85.2g propylene oxide were added to stabilize the starch and the reaction was allowed to proceed for 18 hours at 15 a temperature of 40 to 45°C. The slurry was cooled to 30°C. The slurry was then neutralized to a pH of 5-7 using a 3% solution of hydrochloric acid, washed with distilled water, and air dried.
- 20 70 HA/QUAT starch = 400 g of sodium sulfate and 8 g sodium hydroxide were dissolved in 1500 ml water. 1000 g of 70% high amylose starch were slurried into the aqueous phase with good mixing. 75 g of 3-chloro-2-hydroxypropyl-N,N,N-trimethylammonium chloride were added and the alkalinity adjusted to 20-22 mls of 0.1N HCL (sufficient for a 25 ml sample size to a phenolphthalein end point). The reaction was stirred at a temperature of 45°C for 12-18 hours. The pH was adjusted to 6.0 with 10% HCl and the reaction filtered. The resulting cake was washed with 25 water and air dried. The resulting starch contained 0.24% nitrogen.

The following procedures were used in the examples below.

- Batch cooked dispersion process - The extruded material was suspended at a concentration of 15% by weight in cold (20°F) water. While agitating, the suspension was heated to 97°C using direct steam injection batch cooking in which a steam manifold was placed at the bottom of the cooking vessel and steam was "bubbled" through the suspension. The temperature of the suspension was then maintained at 97°C for a total of 30 minutes. At the end of 30 minutes the dispersed starch was cooled to 65°C and was diluted to 10% by wt. in water for application.
- 10 Note: Although the above method of batch cooking was used in the following examples, other methods of batch cooking exist and are acceptable for dispersing the starches of the present invention. For example, the starch may be mixed into water and placed in a boiling water bath for five minutes with constant stirring, then cooked for an additional 15 minutes with 15 intermittent stirring. The dispersion would then be cooled to 65°C and diluted to 10% by wt. in water for application. The only limitation is that the resultant dispersion be uniform.
- 20 Jet cooked dispersion process - The starch samples were suspended at a concentration of 15% by weight in cold (20°C) water. The suspended starches were then dispersed by continuous steam injection jet cooking in which the starch slurry is pumped into a stream of steam in a "cooking chamber" at a pressure of 67 psia and at a temperature of 148°C. The sample was collected and cooled to 65°C and was diluted to 10% by wt. in water for application.
- 25 Application process
- The dispersed starch was applied to paper at a concentration of 10% by wt. in water at a temperature of 65°C using a modified ETM Multiple System Lab

Coater, manufactured by Euclid Tool and Machine. The technique of application used is generally known as a metered sized press or film transfer size press, in which a "film" of the starch dispersion is applied to two oppositely rotating rolls. The paper passes between the two rolls where the 5 starch film was then transferred to the base paper substrate. After application the paper was dried in an Omega/Arkay photographic drum drier. Application weight onto the paper was determined by weight difference between the untreated paper and the treated paper.

10 Example 1 - Preparation of pregelatinized, chemically modified high amylose starches by extrusion

a. 70 HA/OSA starch was fed into a Werner and Pfleiderer twin-screw co-rotating extruder, Model ZSK-30. The extruder was equipped with a screw 15 having a medium shear screw design, a barrel diameter of 30 mm, two die openings of 3 mm diameter each, a L/D of 21:1, and oil heated barrels set to 180°C in the melt zone. The starch was fed to the extruder at a screw speed of 450 rpm and a rate of 25 kg/hr with input moisture of about 5% based on weight of starch added (residual moisture of starting starch material was 10- 20 14%). The temperature in the extruder was increased to a level of about 190°C. in the barrel or section nearest the die and the extruder pressure was between 200-400 psi.

The product leaving the extruder was collected, allowed to cool, and ground using a commercial multipass grinder (over 95% ground material passed 25 through a 100 mesh A.S.T.M. screen [149 microns]).

- b. Example 1a was repeated using 70 HA/PO starch.
- c. Example 1a was repeated using 70 HA/QUAT starch.

Example 2 - Comparison of extruded chemically modified high amylose starch to jet cooked chemically modified high amylose starch as a paper sizing agent

5 70 HA/OSA starch which was jet cooked was applied to paper. This was repeated with the extruded 70 HA/OSA starch prepared in example 1. The resultant paper was tested for porosity reduction using the standardized Low-Pressure Gurley Density Testing (TAPPI Std. T460 as of 11/92). This test measures the air resistance of paper that permits the passage of 100 cc
10 of air through a paper section covering the orifice of the Gurley Densitometer in 5 to 1800 seconds. The result of this test, when reported as seconds per 100 cc of air per square inch opening, is commonly referred to as Gurley seconds. The results are shown in Table 1, below.

15

Table 1 - Porosity reduction

Starch	Dispersion Method	Gurley (seconds)
70 HA/OSA	Jet cooked	10,500
Extruded 70 HA/OSA	Batch cooked	9,600

Table 1 illustrates the ability of extruded batch cooked high amylose starches to perform substantially the same as samples completely destructured by jet
20 cooking.

Example 3 - Comparison of starches to provide oil and grease resistance to paper

70 HA/OSA starch which was jet cooked was applied to paper. This was repeated with the extruded 70 HA/OSA starch prepared in example 1.

- 5 The resultant paper was tested for oil and grease resistance using the 3M kit. The 3M kit uses TAPPI UM 557 to examine the effects of viscosity and polarity on the ability of the treated paper to resist penetration and wicking of oily substances. The results are shown in Table 2, below.

10

Table 2 - 3M KIT (oil & grease resistance)

Starch	Dispersion Method	Kit Value
70 HA/OSA	Jet cooked	1
Extruded 70 HA/OSA	Batch cooked	1

- Table 2 shows the ability of batch cooked, modified high amylose starch to provide oil and grease resistance surface sizes. The utility of this finding is of particular interest in food packaging where migration of fatty/oily ingredients
15 must be controlled. Examples of this type of applications would be for packaging of candies, popcorn bags and margarine wrapper.

Example 4 - Microscopic evaluation of a variety of jet cooked and extruded high amylose starches

- 20 70 HA starch was extruded as in example 1 and then diluted to 1% solids with cool water. The sample was then placed under a microscope at a magnification of 200 power and an estimation of the amount of undispersed particles was visually determined. This was repeated with the extruded starches of example 1. The results are shown in Table 3, below.

Table 3 - Microscopic Evaluation

<u>Starch</u>	<u>Dispersion Method</u>	<u>% Undispersed</u>
Extruded 70 HA	Batch cooked	>75
Extruded 70 HA/OSA	Batch cooked	5-7
Extruded 70 HA/PO	Batch cooked	<1
Extruded 70 HA/QUAT	Batch cooked	3-5

- 5 The results indicate that a minimum level of substitution was required to provide significant dispersion by batch cooking to be functional as a surface size.

Example 5 - Dispersibility of chemically modified high amylose starches
10 which have been gelatinized using different methods

70 HA/PO starch which was gelatinized by spray drying and the pregelatinized 70 HA/PO starch prepared by extrusion in example 1 were batch cooked. The spray dried 70 HA/PO sample was prepared by a coupled jet cooking/spray drying process conducted at temperatures sufficient to 15 substantially destructure the starch without allowing recrystallization (retrogradation). See for example US 5,131,953. The visual results are shown in Table 4, below.

Table 4 -Pregelatinization Methods

<u>Starch</u>	<u>Observations</u>
Spray dried 70 HA/PO	Clumping, non-homogenous
Extruded 70 HA/PO	Smooth, uniform, fully dispersed

Depending on the method of deconstructing (pregelatinizing), redispersion in water can be difficult and may provide inconsistent materials. As can be seen in table 4 extrusion provides the more consistent, easier to disperse
5 powders from high amylose starches.

Example 6 - Comparison of degree of sizing of a jet cooked and an extruded batch cooked modified high amylose starch

10 70 HA/OSA starch which was jet cooked was applied to paper. This was repeated with the extruded 70 HA/OSA starch prepared in example 1. The resultant paper was tested for degree of sizing using the Hercules Size Test (TAPPI standard T-530 pm-83). An aqueous dye solution is placed on top of a paper and an optical device is used to detect the liquid dye as it moves through the sheet. The optical device measures the time it takes for the reflectance of the paper to drop to 80% of its original value. The results
15 are shown in Table 5, below.

Table 5 - Hercules Test

Starch	Dispersion method	HST seconds
70 HA/OSA	Jet cooked	46.0
Extruded 70 HA/OSA	Batch cooked	46.4
None (blank Sheet)	N/A	3.8

20

Table 5 illustrates the ability of extruded batch cooked high amylose starches surface size paper substantially the same as samples completely destructured by jet cooking.

CLAIMS

We claim:

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1. A substantially pregelatinized, chemically modified high amylose starch, said starch being pregelatinized by extrusion.
2. The starch of claim 1, wherein the chemically modified starch is selected from the group consisting of acetylated, organically esterified, etherified, phosphorylated, inorganically esterified, cationic, anionic, nonionic, zwitterionic, succinate and substituted succinate derivatives of starch.
3. The starch of claim 2, wherein the chemically modified starch is selected from the group consisting of esterified and etherified starches.
4. The starch of claim 2, wherein the chemically modified starch is selected from the group consisting of dodecylsuccinic acid modified starch, octenylsuccinic acid modified starch, propylene oxide modified starch, and quaternary amine modified starch.
5. The starch of claim 4, wherein the starch is modified by octenylsuccinic acid.
- 20 6. The starch of claim 1, wherein the modified starch has a DS of from about 0.01 to 0.5.
7. The starch of claim 6, wherein the modified starch has a DS of from about 0.03 to 0.2.
8. A process of preparing the starch of claim 1 comprising extruding the starch under conditions to substantially pregelatinize the starch.
- 25 9. The process of claim 8, wherein the starch is extruded at a total moisture content of from about 13 to 25%.

10. The process of claim 9, wherein the starch is extruded at a total moisture content of from about 16 to 19%.
11. The process of claim 8, wherein the starch reaches a temperature of about 150 to 250°C in the extruder.
- 5 12. The process of claim 11, wherein the starch reaches a temperature of about 150 to 210°C in the extruder.
13. The process of claim 8, wherein the starch is etherified and reaches a temperature of about 160 to 200°C in the extruder.
14. The process of claim 8, wherein the starch is esterified and reaches a 10 temperature of about 170 to 210°C in the extruder.
15. The process of claim 8, further comprising grinding the extruded starch to a smaller particle size.
16. The process of claim 15, wherein the starch is ground to a particle size of no less than about 60 microns
- 15 17. The process of claim 16, wherein the starch is ground to a particle size of no less than about 100 microns.
18. A composition comprising the starch of claim 1.
19. The composition of claim 18, wherein the composition is paper.
20. A composition comprising the starch of claim 2, said composition being paper.
21. A composition comprising the starch of claim 5, said composition being paper.
22. A composition comprising the starch of claim 7, said composition being paper.
- 25 23. A method of preparing paper comprising applying to the surface of a paper substrate a surface sizing effective amount of the starch of claim 1.

24. A method of preparing paper comprising applying to the surface of a paper substrate a surface sizing effective amount of the starch of claim 2.
25. A method of preparing paper comprising applying to the surface of a paper substrate a surface sizing effective amount of the starch of claim 5.
26. A method of preparing paper comprising applying to the surface of a paper substrate a surface sizing effective amount of the starch of claim 7.
- 10 27. A substantially particle-free dispersion of the starch of claim 1.
28. A substantially particle-free dispersion of the starch of claim 2.
29. A substantially particle-free dispersion of the starch of claim 5.
30. A substantially particle-free dispersion of the starch of claim 7.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/08404

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08B30/14 C08B31/00 C08B33/00 D21H17/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08B D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

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X	US 5 316 578 A (BUEHLER FRIEDRICH S ET AL) 31 May 1994 (1994-05-31) claims 1-30; examples 1-4 -----	1-18
X	EP 0 545 278 A (INVENTA AG) 9 June 1993 (1993-06-09) claim 1; example 1 ----- -/-	1,2,8

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/08404

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 254 450 A (LACZ DAVID J ET AL) 19 October 1993 (1993-10-19) cited in the application claim 1 ---	18-26
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